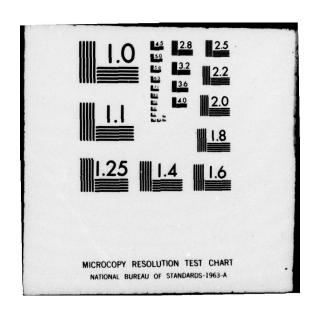
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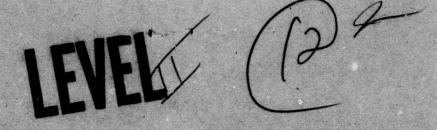
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FJSRL TECHNICAL REPORT - 78-0013 DECEMBER 1978

EXPERIMENTAL INVESTIGATIONS OF XEF2
FOR POSSIBLE LASER APPLICATIONS

CAPT RONALD E. CHANNELL
CAPT LARRY P. DAVIS
LT COL KENNETH E. SIEGENTHALER

PROJECT 2303

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#### FJSRL-TR-78-0013

This document was prepared by the Molecular Dynamics Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado. The research was conducted under Project Work Unit Number 2303-F4-02, Chemical Laser Reactants: XeF,. Captain Ronald E. Channell was the Project Scientist in charge of the work.

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tion.

Project Scientist

Director Directorate of Chemical Sciences

FOR THE COMMANDER

N A. LOVING, Lt Colonel, USAF Chief Scientist

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The feasibility of the use of xenon difluoride as the oxidant for an HF or DF chemical laser system was investigated. The basic research that was accomplished to provide information for this study included spectral studies, photodissociation and thermal dissociation of the xenon difluoride. The absorption spectrum of xenon difluoride confirmed the literature result. Attempts to detect radical thermal or photodissociation products via electron spin resonance spectrometry were unsuccessful. Due to these negative results it was concluded

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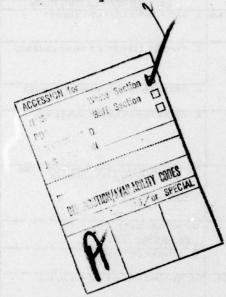
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that xenon difluoride would not be a good candidate for the oxidant in a chemical laser system.



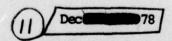
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## PREFACE

This final report documents work done under Work Unit 2303-F4-02, Chemical Laser Reactants: XeF<sub>2</sub>, between 1 December 1977 and 30 September 1978. The authors wish to thank Lt Col Ben A. Loving, Chief Scientist of FJSRL and Capt Barry Crane of AFWL for helpful discussions. In addition, the expert typing of Mrs. Betty Darcy is gratefully acknowledged.

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#### I. INTRODUCTION

This program addressed the problem of developing a safe and storable fluorine source for the operation of chemical or electrical discharge lasers. The laser research community recognized immediately the hazards associated with the use of elemental fluorine even in a "controlled" laboratory research environment. The hazards of handling and using elemental fluorine are such that operational use of the material is not feasible. Thus, the development of laser systems that employ fluorine requires the development of alternate fluorine sources. The reasons for the use of fluorine center around two very attractive characteristics. The reaction of fluorine atoms with deuterium is very exothermic resulting in a large amount of energy potentially available as laser radiation. Secondly, the DF laser radiation is of such a wavelength to be efficiently transmitted through the atmosphere.

The ultimate goal of this program was to achieve a deuterium fluoride (DF) lasing demonstration employing the xenon difluoride-deuterium ( $XeF_2-D_2$ ) system. The information that was to be gained from such a demonstration was threefold: What the spectral transitions were, whether a chain reaction occurred, and thirdly, whether lasing could be achieved using the reactants  $XeF_2$  and  $D_2$ .

The goals were to be achieved through a comprehensive and systematic approach to the spectrophotometry and chemistry associated with the generation of the fluorine atoms and their reaction with deuterium in the XeF<sub>2</sub> system media. This information was to be gained through three phases of technical effort. The first phase was concerned with the

spectral characteristics of XeF<sub>2</sub> in preparation for the photodissociation studies. This phase was accomplished through a thorough literature search plus the collection of experimental data to irrefutably establish the spectral characteristics of XeF<sub>2</sub>. The second phase was to address the kinetics and mechanisms for the photodissociation of XeF<sub>2</sub>. Again, this was accomplished through a thorough literature search plus the necessary experimental research to establish the photodissociation mechanism and kinetics of XeF<sub>2</sub>. The third phase was the determination of the reaction kinetics for the reaction of XeF<sub>2</sub> with deuterium in the gas phase via photo initiation.

Because of manpower limitations and an apparent decrease in interest by the Air Force Weapons Laboratory (AFWL) in the  $XeF_2-D_2$  system, work on the program was terminated prior to achieving the utlimate goal of a  $XeF_2-D_2$  lasing demonstration. The purpose of this report is to summarize the work accomplished on the program to date.

### II. BACKGROUND

The only significant research that has been conducted in this area was performed at the Air Force Rocket Propulsion Laboratory and published in the final report entitled "Chemical Laser Solid Fuels Program",

AFRPL-TR-76-82<sup>1</sup>. The overall objective of this Air Force Rocket Propulsion Laboratory/Air Force Weapons Laboratory interlaboratory program was to demonstrate the feasibility of using solid propellant gas generators to supply the reactants for deuterium fluoride chemical lasers. Several solid fluorine sources were investigated during this program including XeF<sub>2</sub>. The work on XeF<sub>2</sub> was not pursued due to time constraints associated with thoroughly characterizing the XeF<sub>2</sub> solid propellant system (XeF<sub>2</sub> oxidizer and fuel), the relatively low fluorine yield per unit weight of the propellant formulation, and the high molecular weight of the resulting product gases of this propellant system upon combustion.

The program described here dealt with a totally different fluorine system in concept. The approach addressed in this study did not employ the combustion of the XeF<sub>2</sub> oxidizer with a solid fuel to produce fluorine atoms, but rather, produces fluorine atoms by partial photodissociation of the XeF<sub>2</sub> directly. It was theorized that the reaction with D<sub>2</sub> may continue via a chain mechanism involving the undissociated XeF<sub>2</sub>. This would eliminate the large loss of fluorine through reaction with the propellant fuel resulting in a much greater efficiency in fluorine production.

# III. CHEMICAL AND PHYSICAL PROPERTIES OF XENON DIFLUORIDE

Xenon difluoride is an attractive solid fluorine source. It possesses the inherent storability and simplicity of solids plus eliminating the handling hazards associated with elemental fluorine. Xenon difluoride is a stable crystalline compound which can be stored indefinitely in nickel or monel vessels or in thoroughly dried pyrex or silica containers<sup>2</sup>. Exposure to the atmosphere results only in the slow loss of the XeF<sub>2</sub> through sublimation (approximately 0.4 to 0.5 KPa vapor pressure at room temperature, heat of sublimations of 2.9 KJ/mole<sup>2</sup>) or reaction with the atmospheric moisture to produce hydrogen fluoride and xenon. The average bond energy from equilibrium constant data is 7.4 KJ/mole<sup>2</sup> and the heat of formation is 6.2 KJ/mole at 25°C<sup>2</sup>.

Xenon difluoride can be handled much more easily than elemental fluorine. Also, the equilibrium vapor pressure of XeF<sub>2</sub> can be used to readily control the quantity of XeF<sub>2</sub> in the vapor phase by controlling the temperature of the sample container. The relatively low Xe-F bond energy indicates that fluorine atoms can be readily produced by supplying the proper energy for photodissociation. Such characteristics are very attractive for laser systems. Also, the other reaction product, xenon, is a very slow deactivator of vibrationally excited DF<sup>1</sup>. A disadvantage of the presence of xenon is its high atomic weight resulting in low efficiencies of fluorine atom production per unit weight of XeF<sub>2</sub> and the slow kinetics of mixing due to the xenon<sup>1</sup>. The expense associated with the use of xenon compounds appears to be prohibitive. However, a thorough analysis of the situation indicates that the use of lower

grades of xenon (other than research grade), which contains other noble gas compounds that will not readily react with fluorine, drastically reduces the actual cost of the XeF<sub>2</sub> to more reasonable values.

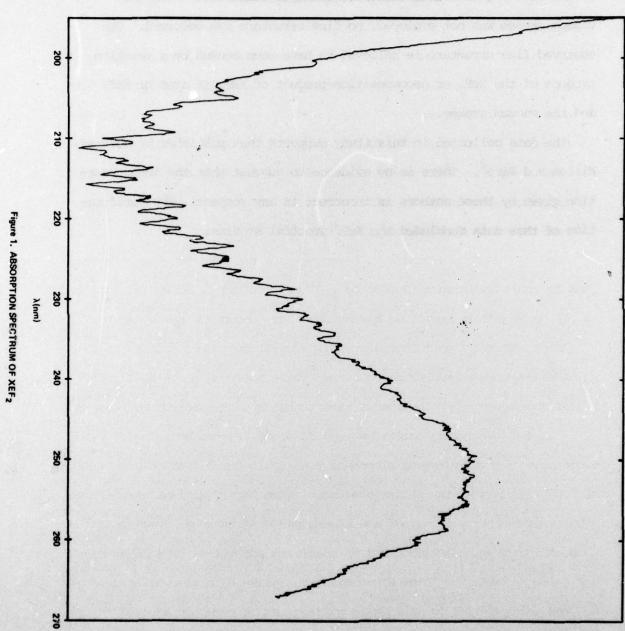
### IV. XENON DIFLUORIDE SPECTRAL STUDIES

As stated in the introduction, the purpose of the XeF, spectral studies was to irrefutably establish the spectral characteristics of XeF, in the gas phase in preparation for the photodissociation studies. A thorough search of the literature indicated that very little work had been devoted to studies of the spectral characteristics of XeF, in the spectral region of interest (2000 to 2500 Å) and no recent work has been concerned with this spectral region. Statements made in the literature<sup>2</sup> suggested that more detailed, high resolution studies were needed to better establish the spectral characteristics of XeF, in the spectral region from 1000 through 3000 A. A recent, detailed, high resolution spectral study of XeF<sub>2</sub> has been reported<sup>3</sup>. Since this study did not address the spectral region from 2000 to 3000 A, a detailed study of XeF, in the gas phase throughout this region was performed on the Carey 15. Initial results indicated (Figure 1) significant fine structure from 2000 to 2600 A. A previous study based on individual measurements as compared to the present continuous scan experiment did not support this observation. The general shape of the absorption curves was very similar. The only noted difference in sample preparation was temperature. In the previously reported experiment<sup>2</sup>, the sample was heated to 22°C. In the experiment reported here the sample was heated to approximately 1.00°C. In an attempt to verify the existence of the observed fine structure and determine its origin, a series of experiments were performed in which the parameters of temperature, heating time, time of the exposure, and pressure were varied. Analysis of the results indicated some unknown

factor was causing the observed fine structure. Suspicion was focused on the vacuum grease used to seal the sample container. When the vacuum grease was not employed, no fine structure was observed. The observed fine structure is believed to have been caused by a reaction product of the XeF<sub>2</sub> or decomposition product of XeF<sub>2</sub> (F atom or XeF) and the vacuum grease.

The data collected in this study supports that published by Jortner, Wilson and Rice<sup>2</sup>. There is no evidence to suggest that the interpretation given by these authors is incorrect in any respect. The verification of this data concluded the XeF<sub>2</sub> spectral studies.

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## V. PHOTODISSOCIATION STUDIES

A 550 watt UV lamp was positioned 48cm from the test cavity. (When positioned closer than 48cm the lamp was affected by the magnetic field of the Electron Spin Resonance Instrument.) A small amount of XeF<sub>2</sub> (less than 1g) was placed inside an ESR tube. The ESR tube was then placed inside a quartz dewar. A strong ESR signal was obtained in the region where normal organic radicals were observed. The light was then switched off and on several times to correlate the UV light source with the radical production. The ESR signal did change with the light intensity. The XeF<sub>2</sub> was removed from the ESR tube and the ESR signal remained the same. Next, the ESR tube was removed and the ESR signal remained the same. It appears the ESR signal was a result of the UV light producing radicals in the quartz dewar. (The quartz dewar was already in place for use in the thermal studies.)

The results of these photodissociation studies was that no radicals were detected when solid  $XeF_2$  was irradiated with UV light.

# VI. THERMAL DISSOCIATION STUDIES

Thermal dissociation studies were conducted while heating the sample from 23°C to 47°C, at 70°C, at 90°C, at 115°C, and at 140°C. Next the sample was inserted into a preheated 152°C sample chamber. The sample consisted of approximately 0.5g of XeF<sub>2</sub> contained in a quartz tube closed off at about 3cm from the bottom. This assured the proper positioning of the sample. When the sample was removed after testing at 152°C, the XeF<sub>2</sub> had liquified. A Varian V4502 Electron Spin Resonance Instrument was used to detect any product radicals resulting from thermal dissociation. The instrument was operated near its sensitivity limit. No radicals were detected on any of the studies.

No radicals due to thermal dissociation were detected when XeF<sub>2</sub> was heated to 152°C. There is a possibility that radicals were formed in quantities only detectable with a more sensitive ESR instrument. Even though the XeF<sub>2</sub> liquified it appeared to return to the original solid crystalline XeF<sub>2</sub> upon cooling. No apparent thermal decomposition was detected.

# VII. CONCLUSIONS AND RECOMMENDATIONS

The spectral studies of XeF<sub>2</sub> confirmed the reported spectrum in the literature. An unexplained fine structure superimposed on the XeF<sub>2</sub> absorption spectrum may have been due to reaction of the XeF<sub>2</sub> with vacuum grease in the cell.

No radicals were detected with ESR from either heating  $XeF_2$  or photolysis of  $XeF_2$  with UV light. It appears that either thermal initiation or photoinitiation of an  $XeF_2$ -D<sub>2</sub> laser may not be possible.

Because of the negative results, manpower limitations, and an apparent decrease in interest in this system by AFWL, it is not advantageous for FJSRL to continue work in this area. If AFWL interest were to increase again, further studies could include an attempt to react  $XeF_2$  with  $H_2$  or  $D_2$  and follow the reaction kinetics.

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